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A biomass burning source of C₁–C₄ alkyl nitrates

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[1] We report the first observations of the emission of five C₁–C₄ alkyl nitrates (methyl-, ethyl-, *n*-propyl-, *i*-propyl-, and 2-butyl nitrate) from savanna burning. Average alkyl nitrate mixing ratios in the immediate vicinity of three bushfires in Northern Australia were 47–122 times higher than local background mixing ratios. These are the highest alkyl nitrate mixing ratios we have ever detected, with maximum mixing ratios exceeding 3 ppbv for methyl nitrate. Methyl nitrate dominated the alkyl nitrate emissions during the flaming stage of savanna burning, whereas C₂–C₄ alkyl nitrates were mostly emitted during the smoldering stage. To explain the formation of alkyl nitrates from biomass burning, we propose a reaction mechanism involving the combination of reactive radicals at high temperature. Bearing in mind the uncertainties associated with extrapolating small data sets to much larger scales, alkyl nitrate emissions from global savanna burning are estimated to be on the order of 8 Gg/yr.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks.
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1. Introduction

[2] Alkyl nitrates (RONO₂) are an important component of the reactive odd nitrogen (NO_y) budget and they can serve as a reservoir for the long-range transport of nitrogen oxides (NO_x = NO + NO₂). In the troposphere the concentration of NO_x controls ozone (O₃) production and influences the oxidizing capacity [Talbot *et al.*, 2000]. Whereas alkyl nitrates typically comprise less than 10% of NO_y within continental air masses [Buhr *et al.*, 1990; Shepson *et al.*, 1993], they comprise a major component (20–80%) of NO_y in the equatorial marine boundary layer over the Pacific [Talbot *et al.*, 2000; Blake *et al.*, 2002].

[3] The two known pathways for alkyl nitrate production are marine emissions [Atlas *et al.*, 1993; Blake *et al.*, 2002; Chuck *et al.*, 2002] and photochemical oxidation of parent hydrocarbons [Darnall *et al.*, 1976]. Here we use air samples collected near active bushfires to investigate biomass burning as a potential source of alkyl nitrates. Biomass

burning is a significant anthropogenic source of carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), nitrous oxide (N₂O), methyl halides, nonmethane hydrocarbons (NMHCs) and sulfur compounds [Andreae and Merlet, 2001 and references therein]. Although Friedli *et al.* [2001] detected enhancements of C₁–C₅ alkyl nitrates from fires in temperate forests and sage scrub regions of the United States, the RONO₂ formation was proposed to occur via the known photochemical mechanism of alkyl radical reaction with oxygen and nitric oxide (NO). In our study, this mechanism does not explain the observed alkyl nitrate enhancements, and an alternative reaction mechanism is proposed. Alkyl nitrate emission ratios relative to CO₂ and CO are calculated, and the emissions are discussed in terms of their impact on local and regional NO_y budgets.

2. Experimental

[4] The alkyl nitrate measurements were made at ground level in Arnhem Land, Northern Australia from Sept. 4–9, 1999. Thirty-five whole air samples were collected in conditioned, evacuated 2-L stainless steel canisters within 3 m of three bushfires, two near Katherine (13°74'S, 131°73'E), and one further northeast in Arnhem Land (13°18'S, 133°58'E). Six additional air samples were collected in remote coastal and inland locations (Cairns, Jaibaru and Alice Springs) to determine local background mixing ratios. The samples were returned to the University of California, Irvine (UCI) and analyzed for alkyl nitrates, CO₂, CO, CH₄, NMHCs, halocarbons, and sulfur gases within two months of sample collection. Our group routinely performs canister integrity studies to ensure that the mixing ratios in the canisters remain stable between sample collection and analysis. During this study, an additional consideration is the freshness and high reactivity of the combustion emissions. Reactive gases such as NO and the hydroxyl radical (OH) do not survive for longer than a few minutes in our canisters, and the formation of alkyl nitrates inside the canisters is very unlikely.

[5] Carbon dioxide was analyzed using gas chromatography (GC) with thermal conductivity detection (TCD), and CO using GC with flame ionization detection (FID). Methyl nitrate (MeONO₂), ethyl nitrate (EtONO₂), *n*-propyl nitrate (*n*-PrONO₂), *i*-propyl nitrate (*i*-PrONO₂), and 2-butyl nitrate (2-BuONO₂) were measured using GC with electron capture detection (ECD). The sample air was preconcentrated in tubing immersed in a liquid nitrogen bath, then revolatilized using a hot water bath and reproducibly split into five streams, with each stream directed to a different

Table 1. Alkyl Nitrate Mixing Ratios (± 1 Standard Error) During the Northern Australia Fire Study, a Karachi City Study, and a Study in the Marine Boundary Layer Over the Equatorial (Eq.) Pacific

Compound	Mixing Ratio (pptv)							
	Northern Australia						Eq. Pacific	
	Bkgd. (<i>n</i> = 6)	Fire (<i>n</i> = 35)	Flaming (<i>n</i> = 20)	Smoldering (<i>n</i> = 15)	Sample 1365	Sample 3819	Karachi (<i>n</i> = 50)	Eq. Pacific (<i>n</i> = 378)
MeONO ₂	5.4 \pm 0.2	569 \pm 158	629 \pm 228	489 \pm 218	3,297	1,246	6.9 \pm 1.9	9.2 \pm 5.1
EtONO ₂	1.7 \pm 0.1	87 \pm 24	60 \pm 21	122 \pm 46	513	562	11.8 \pm 2.2	2.7 \pm 1.8
<i>n</i> -PrONO ₂	0.3 \pm 0.1	14 \pm 4	8 \pm 3	22 \pm 9	69	131	4.7 \pm 0.9	0.1 \pm 0.1
<i>i</i> -PrONO ₂	1.3 \pm 0.2	159 \pm 61	70 \pm 27	277 \pm 135	207	1,961	21.1 \pm 4.6	0.8 \pm 0.6
2-BuONO ₂	0.4 \pm 0.1	37 \pm 13	23 \pm 12	56 \pm 27	63	411	26.0 \pm 7.1	0.1 \pm 0.1

During the fire study, sample 1365 showed the highest MeONO₂ mixing ratio and sample 3819 had the highest C₂–C₄ alkyl nitrate mixing ratios. ‘*n*’ = number of samples.

column-detector combination. The alkyl nitrates were analyzed using Restek1701/ECD and DB5-Restek1701/ECD combinations. For MeONO₂, EtONO₂ and *i*-PrONO₂, both combinations yielded comparable mixing ratios (slopes of 1.08, 0.91 and 1.07 for MeONO₂, EtONO₂ and *i*-PrONO₂, respectively), and the results were averaged to give a single mixing ratio for each alkyl nitrate. The Restek1701/ECD results were not used for *n*-PrONO₂ nor 2-BuONO₂ because of co-elution problems.

[6] The alkyl nitrate measurements were calibrated using two whole air working standards that were analyzed every four samples and have been previously calibrated against a synthetic standard prepared at NCAR. Because the ECD response may not be linear at high mixing ratios, we instead injected a small sub-sample and then scaled the area under the chromatographic peak up to the proper pressure/volume. The alkyl nitrate detection limit is 0.02 pptv. The accuracy of our measurements is 10–20% for alkyl nitrates, 5–7% for CO, and 3% for CO₂. The measurement precision is 2% for alkyl nitrates in the 1–10 pptv range (improving with increasing mixing ratio), 4 ppbv for CO and 2% for CO₂.

3. Results and Discussion

3.1. Mixing Ratios and Emission Ratios

[7] The alkyl nitrate mixing ratios in the savanna burning samples were strongly enhanced relative to background levels (Table 1). For example the average MeONO₂ mixing ratio for the 35 bushfire samples was 105 times higher than the average local background mixing ratio. The alkyl nitrate mixing ratios from this study are also larger than mixing ratios we have measured both in cities and over productive oceanic regions (Table 1). In Karachi, Pakistan our group measured average C₁–C₄ alkyl nitrate mixing ratios ranging from 4.7–26.0 pptv [Barletta *et al.*, 2002]. Over productive regions of the equatorial Pacific, we have recorded maximum C₁–C₄ alkyl nitrate mixing ratios of 50 pptv [Blake *et al.*, 2002]. The maximum C₁–C₄ alkyl nitrate mixing ratios measured during the Australian fire study are the highest we have ever recorded, ranging from 130–3300 pptv.

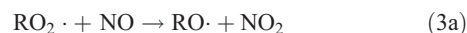
[8] Trace gas emissions from biomass burning are often expressed as emission ratios (ERs), the excess mixing ratio of trace gas *X* (plume–background) divided by the excess mixing ratio of a reference compound such as CO₂ or CO. Trace gas emission during biomass burning is a function of factors including combustion efficiency (CE; $\Delta\text{CO}/\Delta\text{CO}_2$) and fuel composition [Lobert *et al.*, 1991; Elvidge *et al.*, 1996]. A $\Delta\text{CO}/\Delta\text{CO}_2 < 0.1$ ppmv/ppmv indicates a high CE (flaming), whereas $\Delta\text{CO}/\Delta\text{CO}_2 > 0.1$ ppmv/ppmv

reflects a low CE (smoldering) [Bonsang *et al.*, 1995]. For the 35 samples collected in Arnhem Land, 20 were identified as flaming samples (CO₂ = 2016 \pm 432 ppmv; CO = 109 \pm 30 ppmv) and 15 as smoldering samples (CO₂ = 2242 \pm 566 ppmv; CO = 587 \pm 205 ppmv). In this paper, CO₂ is used as the reference compound for flaming samples, and CO for smoldering samples.

[9] Like CO, many trace gases are produced in reduced chemical states predominantly in the smoldering stage [Blake *et al.*, 1996]. Consistent with this, the C₃–C₄ alkyl nitrates showed a much better correlation with CO during the smoldering stage than with CO₂ during flaming (Table 2). Their ERs were 7–13 times higher in the smoldering samples as compared to flaming. Interestingly, MeONO₂ showed a much better correlation with CO₂ during the flaming stage than with CO during smoldering. The magnitude of the MeONO₂ ER was similar during both fire stages. Ethyl nitrate showed intermediate characteristics in which it strongly correlated with both CO₂ and CO during the flaming and smoldering stages, respectively. The ER for EtONO₂ was five times higher during smoldering than during flaming.

3.2. Proposed Formation Mechanism

[10] The known photochemical pathway for the formation of alkyl nitrates is [Darnall *et al.*, 1976]:



where RH is a parent hydrocarbon, R is an alkyl radical, RO₂ is an alkyl peroxy radical, and RO is an alkoxy radical.

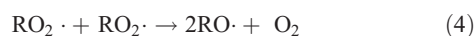
Table 2. Emission Ratios (ERs) of Alkyl Nitrates Relative to CO₂ (flaming) and CO (Smoldering), Respectively, During the Northern Australia Fire Study

Compound	Flaming ER (ppmv/ppmv)		Smoldering ER (ppmv/ppmv)	
		<i>r</i> ²		<i>r</i> ²
MeONO ₂	$[4.7 \pm 0.5] \times 10^{-7}$	0.81	$[6.8 \pm 2.3] \times 10^{-7}$	0.40
EtONO ₂	$[4.2 \pm 0.6] \times 10^{-8}$	0.72	$[2.0 \pm 0.3] \times 10^{-7}$	0.77
<i>n</i> -PrONO ₂	$[4.9 \pm 1.2] \times 10^{-9}$	0.49	$[4.0 \pm 0.5] \times 10^{-8}$	0.82
<i>i</i> -PrONO ₂	$[4.5 \pm 1.0] \times 10^{-8}$	0.54	$[5.7 \pm 0.9] \times 10^{-7}$	0.75
2-BuONO ₂	$[1.6 \pm 0.5] \times 10^{-8}$	0.36	$[1.1 \pm 0.2] \times 10^{-7}$	0.67

The uncertainty estimates represent $\pm 1\sigma$.

However, this mechanism does not explain the magnitude and pattern of the observed alkyl nitrate enhancements. In particular, the photochemical processing times were too short to account for the observed MeONO₂ enhancements, even with the high levels of OH that are expected in biomass burning plumes [Foberich *et al.*, 1996], and the very high levels of CH₄ that were present (7.3 ± 2.6 ppmv during flaming; 39 ± 14 ppmv during smoldering).

[11] To explain the formation of alkyl nitrates during biomass burning, we propose a mechanism similar to equations (1)–(3b), but with RO reacting with NO₂ to form RONO₂, rather than RO₂ with NO. Following the formation of RO₂ via equations (1)–(2), we propose that RO is quickly formed because of the abundance of radicals in the fire. The decomposition of larger RO molecules forms smaller, more stable RO radicals, which then quickly react with NO₂ to form RONO₂ ($k \sim 10^{-11}$ cm³ molec⁻¹ s⁻¹; DeMore *et al.*, 1997):



[12] By this pathway, the formation of an alkyl nitrate is not constrained by its RH + OH rate constant nor by its RO₂ + NO branching ratio (both of which are very small for MeONO₂ compared to the heavier alkyl nitrates), consistent with the relatively large amounts of MeONO₂ that were observed. The experimental data further corroborate this proposed mechanism because of the high correlation between MeONO₂ and CO₂ during the flaming stage of the fire in which temperature (*T*) and mixing ratios of NO_x and short, stable radicals are the highest ($T > \sim 950$ K during the flaming stage. By contrast, the formation of longer radicals is favoured during the cooler smoldering stage [$T < \sim 850$ K; Crutzen and Goldammer, 1993], which is consistent with the better correlation of C₃–C₄ alkyl nitrates with CO than with CO₂.

3.3. Global Significance

[13] Despite the very high alkyl nitrate mixing ratios that were observed, the absolute magnitudes of their ERs are relatively small (Table 2). The ERs of ethane and the biomass burning tracer methyl chloride (CH₃Cl) relative to CO during smoldering were 3–5 orders of magnitude larger [$(4.0 \pm 0.6) \times 10^{-3}$; and $(4.0 \pm 0.9) \times 10^{-4}$ ppmv/ppmv, respectively]. These CH₃Cl and ethane ERs are comparable to those reported by Blake *et al.* [1996] for Brazilian and African savanna fires. By comparison, the alkyl nitrate ERs for the smoldering samples are 4–11 times smaller than those reported relative to CO by Friedli *et al.* [2001] from North American wildfires. The reason for this difference is not clear, but could be related to different fuel composition. We note that in the case of the North American fires, a much smaller range of RONO₂ and CO mixing ratios was observed.

[14] Savanna fires are the single largest global source of biomass burning emissions [Andreae *et al.*, 1996], and the ERs measured here can be used to estimate the annual alkyl nitrate release from global savanna burning and all types of

Table 3. Estimated Alkyl Nitrate Emissions From Global Savanna Fires and From All Types of Biomass Burning Worldwide

Compound	Global Savanna Burning Emissions		Global Biomass Burning Emissions	
	Flaming (Gg/yr)	Smoldering (Gg/yr)	Flaming (Gg/yr)	Smoldering (Gg/yr)
MeONO ₂	5.0	0.4	11.2	1.4
EtONO ₂	0.5	0.1	1.1	0.5
<i>n</i> -PrONO ₂	0.1	0.03	0.2	0.1
<i>i</i> -PrONO ₂	0.7	0.5	1.5	1.6
2-BuONO ₂	0.3	0.1	0.6	0.3
Total RONO ₂	6.6	1.2	14.6	3.9

The uncertainty in individual estimates is at least a factor of 2.

biomass burning. Such calculations assume that the ERs from the three Australian savanna fires are representative of savanna burning and biomass burning in general, whereas ERs for individual trace gases vary with factors including CE and fuel composition (see above). Here we did not sample prefire fuel nor postfire ash, and we cannot report directly on fuel composition. However, Hurst *et al.* [1994] performed detailed analyses of the mass, carbon and nitrogen loads for fuel and ash in a nearby region of the Australian Northern Territory (12°S, 132°E). The reader is referred to this paper for detailed findings.

[15] Bearing the above assumptions in mind, global alkyl nitrate emissions from biomass burning were estimated using the measured ERs and the amounts of CO₂ and CO released annually from global savanna burning (6,070 Tg CO₂ yr⁻¹ and 232 Tg CO yr⁻¹) and all types of biomass burning (13,500 Tg CO₂ yr⁻¹ and 748 Tg CO yr⁻¹) [Andreae *et al.*, 1996; Holloway *et al.*, 2000]. The uncertainties in the CO₂ and CO estimates are at least a factor of two [Andreae *et al.*, 1996]. Based on these values, global savanna burning emissions for the five C₁–C₄ alkyl nitrates reported here are estimated to total roughly 6.6 Gg/yr (mainly as MeONO₂) during the flaming stage, and 1.2 Gg/yr (mainly as C₂–C₄ alkyl nitrates) during the smoldering stage, for a total on the order of 8 Gg/yr (Table 3). For global biomass burning, summed C₁–C₄ alkyl nitrate emissions on the order of 18 Gg/yr are estimated. In both cases, MeONO₂ emissions during the flaming stage comprise a majority (roughly two-thirds) of the total C₁–C₄ alkyl nitrate emissions.

[16] The MeONO₂ emissions from savanna and global biomass burning are estimated to total roughly 5.4 and 12.6 Gg/yr, respectively (Table 3). By comparison, for an atmosphere of about 1.7×10^{20} moles of air, a globally averaged MeONO₂ mixing ratio of roughly 2 pptv, and a global MeONO₂ lifetime of 0.1 yr, the global MeONO₂ source is calculated to be on the order of 300 Gg/yr. That is, MeONO₂ released from global biomass burning likely accounts for only a small portion ($\sim 4\%$) of the global MeONO₂ source.

[17] Likewise, the global release of alkyl nitrates from savanna burning (1.3 Gg N yr⁻¹) is small compared to the amount of NO_x that is emitted [1.1 Tg N yr⁻¹; Granier *et al.*, 1996]. However, alkyl nitrates have a relatively low reactivity compared to other components of the NO_y budget, and RONO₂ to act as a reservoir for the long-range transport of NO_x. In particular, MeONO₂ is the longest-lived of the alkyl nitrates, and MeONO₂ emissions from biomass burning are a previously unknown source for the transport of NO_x to downwind locations. In very aged

biomass burning plumes, however, we have previously noted a lack of MeONO₂ enhancement [Blake *et al.*, 1999]. This is likely a result of relatively low MeONO₂ ERs coupled with long transport times during which MeONO₂ can become depleted (thereby releasing NO_x) as a result of photochemistry, and diluted as a result of atmospheric mixing.

4. Conclusions

[18] Savanna biomass burning fires are major point sources of C₁–C₄ alkyl nitrates. Average alkyl nitrate mixing ratios in the immediate vicinity of three Northern Australian bushfires are the highest we have ever detected, exceeding maximum mixing ratios we have measured both in city studies and over productive oceanic regions. Despite these high mixing ratios, the alkyl nitrate ERs are small compared to those of various NMHCs and of the biomass burning tracer CH₃Cl. Methyl nitrate showed the highest alkyl nitrate ER, and its ERs relative to CO₂ (flaming) and CO (smoldering) were of similar magnitude. The C₂–C₄ alkyl nitrates showed ERs were 5–13 times higher during smoldering than during flaming. The magnitude and pattern of the alkyl nitrate enhancements cannot be explained by the traditional photochemical production mechanism, and we suggest that the alkyl nitrates were formed by RO + NO₂ reaction, rather than RO₂ + NO.

[19] Methyl nitrate emissions during the flaming stage contribute about two-thirds of the total estimated alkyl nitrate emissions during savanna and global biomass burning. However, biomass burning likely has a small impact on the global MeONO₂ budget. Similarly, global alkyl nitrate emissions from savanna fires are small in comparison to the amount of NO_x that is released. Notwithstanding, the very high mixing ratios measured close to the fires (up to 3.3 ppbv of MeONO₂) suggest that alkyl nitrate release during biomass burning likely impacts the reactive nitrogen budget in remote regions with few local NO_x sources.

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